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Sensitive capillary electrophoresis microchip determination of trinitroaromatic explosives in nonaqueous electrolyte following solid phase extraction

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Abstract

A capillary electrophoresis (CE) microchip is utilized for the sensitive separation and detection of three trinitroaromatic explosives: 1,3,5-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrophenyl-N-methylnitramine (tetryl), in the presence of 10 other explosives and explosive derivatives in nonaqueous electrolyte (acetonitrile/methanol 87.5/12.5 (v/v), 2.5 mM NaOH, 1 mM sodium dodecyl sulfate (SDS)). The chemical reaction of bases, e.g. hydroxide or methoxide ions, with trinitroaromatic compounds forms red colored derivatives that can be easily detected using a green light emitting diode (LED) on the microchip. Two surfactants bearing opposite charge, cetyltrimethylammonium bromide (CTAB) and SDS are compared with respect to their effect on separation times, detection limits and resolving powers for separating these explosives. All microchip separations were achieved in <20 s. In the absence of solid phase extraction (SPE), the detection limits obtained for the trinitroaromatic explosives were as follows: TNB, 60 µg/l; TNT, 160 µg/l and tetryl, 200 µg/l. By coupling the microchip separation with ex situ SPE, the detection limits for detecting these three explosives in seawater were lowered by 240 to more than 1000 times: TNB, 0.25 µg/l; TNT, 0.34 µg/l and tetryl, 0.19 µg/l.

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Keywords: Capillary electrophoresis; Microchip; Explosives; Solid phase extraction; Nonaqueous

1. Introduction

Due to the many advantages associated with glass microchip separations, including portability, minimal waste generation, rapid separation times, small sample size requirements, ease of integration and low cost, there has been significant recent activity in applying

capillary electrophoresis (CE) microchip separations to the detection of explosives [1–3]. Development of a rapid, portable and selective monitor for different explosive residues is of interest to environmental land and sea remediation efforts, forensic analysis following terrorist or other criminal activity, and land mine and underwater unexploded ordnance identification for the military. Wang et al. was the first to demonstrate the separation of five different explosives and explosive degradation products on a glass microchip utilizing micellar electrokinetic chromatography and

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amperometric detection on a screen-printed carbon line electrode [1]. Wallenborg and Bailey utilized indirect fluorescence detection and identical micellar electrokinetic conditions to separate 10 different explosives and explosive degradation products [2]. In addition, a gold film electrochemical detector prepared by electroless deposition onto the capillary outlet of a glass microchip was demonstrated by Hilmi and Luong to give superior detection limits for trinitrotoluene (TNT) down to 24 µg/l in a separation from three other degradation products [3]. In this study, we report the first CE microchip separation of trinitroaromatic explosives in a complex mixture of explosives and explosive derivatives in nonaqueous electrolyte (acetonitrile/methanol 87.5/12.5 (v/v), 2.5 mM NaOH, 1 mM sodium dodecyl sulfate (SDS)). To demonstrate the applicability of this technique, trace levels of trinitroaromatic explosives dissolved in seawater are preconcentrated via ex situ solid phase extraction (SPE) and analyzed on the microchip.

The interaction of bases, e.g. hydroxide or methoxide (CH_3O^-) ions, with nitroaromatic compounds is known to form red to violet colored derivatives [4–6]. Studies with TNT indicate that several possible products may be formed, depending on the solvent composition and the ratio of TNT to base [7–10]. A field screening test for TNT was developed by Medary, which takes advantage of this color producing reaction in methanol to give detection limits for TNT in soil in the 4–8 mg/l range [11]. Our studies have shown that TNT reacts with base form a more intensely colored product in basic acetonitrile (MeCN) solution, than in basic aqueous or methanol solution.

Another benefit of using acetonitrile is its direct applicability to solid phase extraction procedures for explosives. Traditionally, the extraction (or preconcentration) of explosives in the field has relied upon SPE methods, utilizing organic polymer resins or reversed-phase silicas. These materials are capable of strongly adsorbing and concentrating explosives for subsequent elution into a solubilizing organic medium such as acetonitrile [12]. The extraction efficiency of this approach for organic explosives such as TNT and DNT is essentially 100%, with concentration factors as high as 100 times [13]. In order for a microchip separation technique for nitroaromatic explosives to fully exploit the high concentration factors afforded by SPE methods, it is important that the separation

operate in a nonaqueous electrolyte. Direct incorporation of SPE methods onto a microchip has been demonstrated viable by Harrison and co-workers [14] and Ramsey and co-workers [15]. Ramsey and co-workers utilized C18 coated microchannels for enriching and subsequently eluting a neutral dye. Harrison utilized two weirs within a sample channel for trapping octadecylsilane coated silica beads on a microchip for subsequent extraction studies of the dye BODIPY from water into acetonitrile. In this study, we investigate the ex situ SPE of explosives from seawater into acetonitrile and the subsequent application of this nonaqueous sample to the microchip.

Acetonitrile has been successfully utilized in numerous CE separations, including dye substances [16], polycyclic aromatic hydrocarbons [17] and chlorinated phenolic compounds [18]. To date, there has been only one reported example of a pure nonaqueous phase separation performed on a microchip platform [19], although several have utilized solvent programming of organic/aqueous buffers [14,20]. Pure acetonitrile was shown by Wright et al. to have an electroosmotic mobility in CE that is more than three times that of a pH 9 borate buffer [21]. This attribute can lead to substantially faster separation times on a microchip. Because acetonitrile has a significantly lower conductivity compared to aqueous electrolyte systems, deeper microchannels (100 µm versus typical 20 µm channels) can be employed, permitting simple absorbance measurements to be made with an light emitting diode (LED) [22,23].

2. Experimental section

2.1. Reagents

o-Nitrotoluene (*o*-NT), *m*-nitrotoluene (*m*-NT), *p*-nitrotoluene (*p*-NT), nitrobenzene (NB), *m*-dinitrobenzene (*m*-DNB), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2-amino-4,6-dinitrotoluene (2-amino-4,6-DNT), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrophenyl-*N*-methylnitramine (tetryl) were purchased from Chem Service (P.O. Box 599, West Chester, PA 19381). Anthracene, cetyltrimethylammonium

bromide (CTAB), sodium dodecyl sulfate were obtained from Aldrich, while sterile filtered seawater was obtained from Sigma.

The nonaqueous electrolytes used in the microchip CE were prepared from a mixture (87.5/12.5 v/v) of acetonitrile (MeCN) and methanol (MeOH) containing 2.5 mM NaOH and 0.25–1.5 mM of one of the two surfactants, CTAB or SDS. All nonaqueous electrolytes were freshly made prior to the CE experiments.

2.2. Instrumentation

A Hitachi U-3000 spectrophotometer was used to record the UV–VIS spectra of TNT, TNB, and tetryl in basic nonaqueous electrolytes.

The borofloat microchips utilized in the CE experiments were obtained from Microlyne Inc. in Alberta, Canada. The microchips contain a simple cross pattern, lithographically etched into the glass substrate (approximately 100 µm deep × 200 µm wide) to define the sample loading and separation channels. A glass cover plate pre-drilled to contain four access holes was thermally bonded to the micro-fabricated glass plate. Sample, buffer, and waste reservoirs were constructed by inserting shortened pipette tips into the access holes. The lengths of the loading and separation channels were 10 and 85 mm, respectively with an effective separation length of 80 mm.

The high voltage switching apparatus consisted of two 8 kV high voltage power supplies (Bertan High Voltage Corp., Hicksville, NY, Model PMT-75C) and an array of high voltage reed relays (Crydom, San Diego, CA, Model DAT71210) which were configured to enable remote switching via a LABView interface (National Instruments, Austin, TX) between the separation and floating load modes of operation. Samples were injected electrokinetically using a floating mode of injection, by applying a small potential between the sample reservoir (−260 to −330 V) and a grounded waste reservoir while floating the buffer and buffer waste reservoirs. Subsequently, the high voltage power supply was switched to a negative polarity separation mode with the primary field applied between the buffer and buffer waste reservoirs, while the sample and sample waste reservoirs were held at a potential preventing their electroosmotic flow into the separation microchannel. To avoid any leakage and dilution

of the sample solution and hydrodynamic flow inside the separation channel, factors which are detrimental to the detection sensitivity and separation efficiency, the solutions in all four reservoirs were maintained at the exact same level during the runs. Microchannels were flushed with 1 M HCl, water, methanol and the nonaqueous electrolyte prior to use. The sample solution was prepared by diluting the standard solutions of explosives with the appropriate nonaqueous electrolyte to a concentration of 1–2 mg/l.

Colorimetric detection of TNT, TNB, and tetryl in MeCN/MeOH mixed solvents on the microchip was achieved using an instrumental set-up described previously [24]. A green LED light source (505 nm, Hosfelt Electronics) was oriented directly above the separation channel, as close as possible to the microchannel and the buffer waste reservoir. Light passing through the microchannel was collected using a microscope objective (Newport, 20×) and directed through a perpendicularly oriented, 200 µm × 3 mm rectangular slit onto a miniature, red-shifted photomultiplier tube (Hamamatsu, Model H5783-01). The slit enables the observation of only a small subsection of the magnified microchannel, enhancing resolution. The PMT current was monitored using a 617 Keithley Programmable Electrometer. Peaks in the electropherograms are given in terms of the PMT current and are proportional to the transmittance of the green LED light through the microchip separation channel.

For the electroosmotic flow determinations, 1 mM anthracene was dissolved in the same nonaqueous electrolyte employed for the analysis of the tri-nitroaromatic explosives. Although not an ideal electroosmotic, neutral molecule marker due to its large size and aromaticity, anthracene was utilized for verifying electroosmotic flow direction because of its UV absorption above the 320 nm absorption cutoff defined by the Borofloat glass microchip, itself. A UV light source (190–410 nm, Analytical Instrument System, Model AIS) and a UV-transmissive microscope objective (Newport, U-27x) were used in place of the green LED for the absorptive detection of anthracene.

2.3. Solid phase extraction

A mini-extraction column (0.8 mm i.d., 1.58 mm o.d. Teflon tubing) was packed with 1 mg Lichrolut (EM Science), and conditioned by flushing with 10 ml

MeOH and 20 ml Milli-Q water. A 40 ml aliquot of seawater sample, spiked with 0.5 µg/l each of TNT, TNB, and tetryl, was pumped through the column at 3 ml/min using a Kloehn Model 5300 syringe pump. Prior to eluting the analytes with 17 µl acetonitrile, the column was washed with 5 ml Milli-Q water, in order to dissolve any adsorbed salts, and then dried by pushing air across the column for 1 min at a flow rate of 5 ml/min to remove any excess water. The acetonitrile sample plug was subsequently spiked with an appropriate amount of basic methanol surfactant solution, and then applied to the microchip for analysis.

3. Results and discussion

The visible absorption spectra of *o*-NT, *m*-NT, *p*-NT, NB, *m*-DNB, 2,4-DNT, 2,6-DNT, 2-amino-4,6-DNT, TNB, TNT, HMX, RDX and tetryl were each separately examined in a mixed solvent of MeCN/MeOH (87.5/12.5 (v/v)) containing 2.5 mM NaOH and one of two surfactants, SDS or CTAB. From these spectra, it was determined that only TNT, TNB and tetryl absorb between 400 and 700 nm at a concentration of 10 mg/l or below (see Fig. 1 for the spectra collected in the presence of 1.0 mM SDS). All other explosives and degradation products examined were colorless throughout this wavelength range.

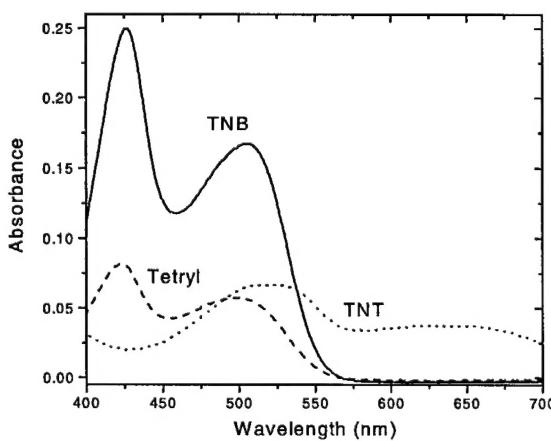


Fig. 1. Visible absorption spectra for 1 mg/l TNT, TNB and tetryl in MeCN/MeOH (87.5/12.5 (v/v)) containing 2.5 mM NaOH and 1.0 mM SDS.

This color formation reaction seems to be especially sensitive to trinitroaromatic compounds, apparently due to the presence of three electron withdrawing nitro groups on the aromatic ring. The reaction product of TNT appears purple in color (molar absorptivity of 7.2×10^3 l/(mol cm)), while those of TNB (molar absorptivity of 3.5×10^4 l/(mol cm)) and tetryl (molar absorptivity of 8.0×10^3 l/(mol cm)) yield a yellowish-brown color. The spectra obtained in the absence of SDS or presence of CTAB were very similar to those shown in Fig. 1. The colored products formed in these buffers were relatively stable; no significant change in the absorption spectrum was observed over the course of 1 h, although the color diminished after standing overnight.

The colored product formed from the reaction of TNT with base is the monoanion shown in Fig. 2, a product which arises from the deprotonation of the methyl group, as Fyfe et al. have demonstrated [10]. The colored products formed from the reactions of TNB and tetryl with base are the monoanions formed by the addition OH^- or OCH_3^- to the aromatic ring

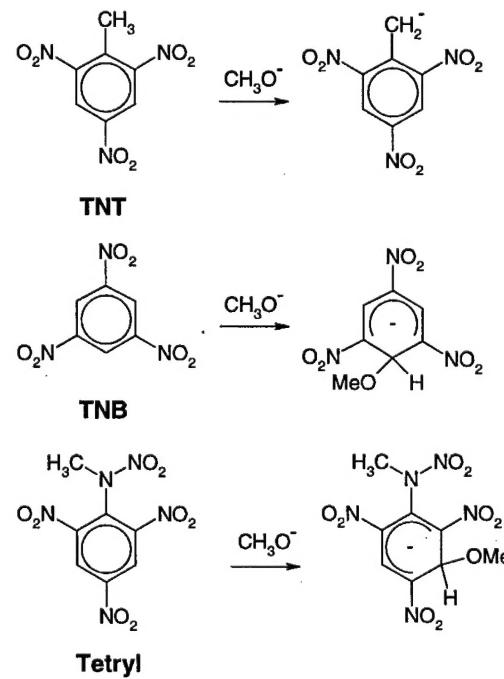


Fig. 2. Chemical reaction of TNT, TNB and tetryl in basic MeCN/MeOH.

(see Fig. 2). These assignments have been made based upon previous investigations by Fyfe et al. [10] and Bernasconi [25]. Each of these colored derivatives has a strong absorption band near 500 nm, thereby, permitting a 505 nm green LED to be utilized as the light source for absorbance detection on a glass microchip. Although not pursued here, it is interesting to note that by choosing an LED light source whose output is between 650 and 700 nm, only TNT would be detectable on the microchip, allowing the application of longer injection times to compensate for the loss in sensitivity at this monitoring wavelength. The use of an LED light source, in contrast to many lasers, enables a small, compact, inexpensive, low power, reasonably narrow wavelength light source to be used that will maintain the portable possibilities inherent with the glass microchip.

Acetonitrile was the nonaqueous electrolyte of choice for performing this separation due to its amenability to both CE and SPE, in addition to improved sensitivity for the colorimetric detection of trinitroaromatics in basic acetonitrile when compared to basic methanol solution, for example. Sodium hydroxide is insoluble in pure acetonitrile, however, and so various mixed buffer compositions of MeCN/MeOH were investigated on the microchip. An interesting phenomenon was observed on the microchip with respect to the direction of electroosmotic flow, and this phenomenon was correlated to the concentration of MeOH in the buffer and the corresponding effect this has on the solubility of NaOH. For buffer compositions containing 2.5 mM NaOH in <15% MeOH in MeCN, the NaOH forms a colloidal suspension, which precipitates after allowing to sit overnight. When a freshly prepared solution was applied to the microchip, studies with anthracene as a neutral electroosmotic marker indicated a reversal in the electroosmotic flow direction. We are currently investigating this phenomenon, in particular, assessing whether this reversal can be ascribed to the excess common ion effect of Na^+ ions surrounding the colloidal NaOH(s) particles and the interaction of these particles with the microchannel wall. The addition of surfactant to our nonaqueous electrolyte (0–1.5 mM), on the other hand, had no impact on the electroosmotic flow direction. This is not surprising when we consider that the hydrophobic interaction of surfactants will be significantly reduced in nonaque-

ous electrolyte. This reversal in electroosmotic flow permitted the application of a negative potential to the buffer reservoir, significantly shortening separation times for the anionic trinitroaromatic explosives.

Initial microchip separations were carried out in MeCN/MeOH mixed solvents containing NaOH, but in the absence of any surfactant. By varying the concentration of NaOH and the ratio of MeCN to MeOH while monitoring the separation of TNT, TNB and tetryl, the composition of MeCN/MeOH (87.5/12.5 (v/v)) containing 2.5 mM NaOH was determined to give the best results in terms of reproducible separation times and reasonable separation currents on the microchip (<30 μA). When using this nonaqueous electrolyte, a negative potential field applied to the buffer reservoir was required to enable the transport and separation of the negatively-charged explosive derivatives. Despite all efforts, however, TNB and tetryl could not be separated in the absence of a surfactant. As we can see from Fig. 3a, the separation is extremely rapid (<20 s), and assuming TNT is the analyte of interest in a particular assay, this nonaqueous electrolyte would be sufficient to separate TNT from TNB and tetryl.

In order to achieve a complete separation of these three trinitroaromatics, surfactant was added to the aforementioned buffer. Due to the dimensions of the separation channel ($\sim 100 \mu\text{m}$ deep $\times \sim 200 \mu\text{m}$ wide), only low concentrations of surfactant (0.5–1.5 mM)

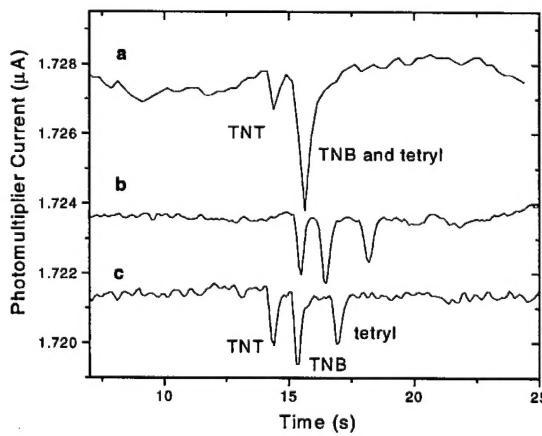


Fig. 3. Effect of surfactant type on the microchip separation of 2 mg/l TNT, 1 mg/l TNB and 2 mg/l tetryl in MeCN/MeOH (87.5/12.5 (v/v)) containing 2.5 mM NaOH: (a) no surfactant, (b) 0.5 mM CTAB, (c) 1.0 mM SDS. Applied separation field strength, -506 V/cm , using a 1 s floating load.

were used in order to avoid excessive Joule heating. At these concentrations, especially in nonaqueous media, the formation of micelles is unlikely, and the separations may be attributed to solvophobic interactions between the analytes and individual surfactant ions [26–28].

CTAB was the first surfactant considered, because its positive charge was expected to help its association with the trinitroaromatic anions. The concentration of surfactant used in these studies ranged from 0.25 to 0.75 mM. Fig. 3b shows the electropherograms obtained when using MeCN/MeOH (87.5/12.5 (v/v)) containing 2.5 mM NaOH and 0.5 mM CTAB at various negative field strengths. In the presence of CTAB, the three trinitroaromatics are detected within 19 s, and are completely resolved from one another with an eluting order of TNT, TNB, and tetryl. However, as the potential is increased from -506 to -688 V/cm (while maintaining the separation current below 30 μ A, Fig. 4), the resolution actually degrades despite a decrease in the peak widths, possibly due to the rapid electroosmotic transport of analytes down the microchannel or the temperature gradient caused by Joule heating. Excessive currents (>30 μ A) were observed when potentials higher than -688 V/cm were applied. Separations utilizing 0.25 and 0.75 mM CTAB were also examined, but the optimal resolution

for separating these three trinitroaromatics was obtained using 0.50 mM CTAB and a separation potential of -508 V/cm. Under these conditions, excellent reproducibility in migration time was achieved, with the relative standard deviation (R.S.D.) in migration time for the three analytes being less than 0.7% ($n = 10$).

In order to understand the effect of oppositely-charged surfactants on the separation of the three anionic explosive derivatives, buffers containing 2.5 mM NaOH and 0.5–1.5 mM SDS (negatively-charged) in a mixed solvent of MeCN/MeOH (87.5/12.5 (v/v)) were used to perform the separation under a similar separation potential of -506 V/cm. Fig. 3 shows the electropherograms obtained for two different surfactants at their optimal concentration: CTAB (0.5 mM, Fig. 3b) and SDS (1.0 mM, Fig. 3c). In both cases, the three analytes maintained the same elution order of TNT, TNB, and tetryl. With regards to separation times, the buffer system containing SDS demonstrated the shortest separation times for all three compounds when compared to CTAB (SDS (1.0 mM): 14.4, 15.3, 16.9 s; CTAB (0.5 mM): 15.5, 16.4, 18.3 s). Table 1 lists the resolution and theoretical plates calculated from these electropherograms.

The separation mechanism in the presence of low surfactant concentrations likely involves a dynamic equilibria between the negatively-charged trinitroaromatic analytes and the monomeric surfactant in solution, with the associated species formed from weak hydrophobic interactions, and from electrostatic attraction in the case of CTAB. For each different surfactant used, the proposed equilibria are presented as follows:



Table 1
Resolution and theoretical plates for the microchip separation of TNT, TNB, and tetryl on a microchip utilizing either surfactant, CTAB or SDS (0.5 mM and 1.0 mM)

Analyte	Resolution (Rs ^a)		Theoretical plates (N ^b)	
	CTAB	SDS	CTAB	SDS
TNT	1.8	2.0	14790	12711
TNB	1.8/3.2	2.0/3.1	16557	14484
Tetryl	3.2	3.1	11595	17603

^a Rs = $(2 \ln 2)^{1/2} (t_{r2} - t_{r1}) / (w_{h1} + w_{h2})$, N = 5.54 $(t_r/w_h)^2$.

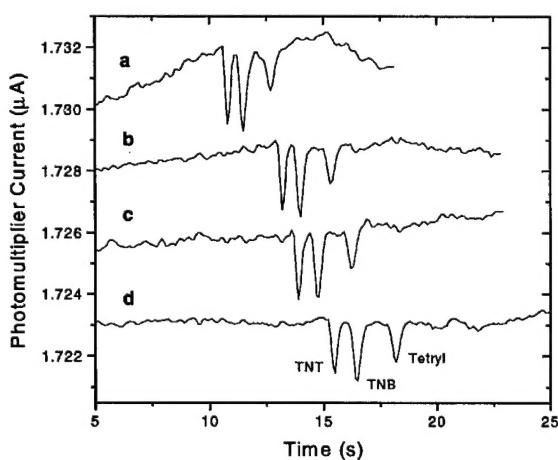


Fig. 4. Effect of separation field strength on microchip separation of 2 mg/l TNT, 1 mg/l TNB and 2 mg/l tetryl in MeCN/MeOH (87.5/12.5 (v/v)) containing 2.5 mM NaOH and 0.5 mM CTAB. Applied separation field strength using a 1 s floating load: (a) -688 V/cm, (b) -631 V/cm, (c) -566 V/cm, (d) -506 V/cm.

Since different explosive derivatives have different polarity, the extent of their interaction with the surfactant will vary, influencing the equilibrium between the associated species and the free analytes in solution. The separation is realized by the difference in net migration time that is defined as the weighted average of the migration time of the free explosive derivative in solution and as an associated species.

Comparing the electropherograms obtained in the presence (Fig. 3c) and absence (Fig. 3a) of SDS, we conclude that there is sufficient hydrophobic interaction between SDS and tetryl to enable a complete separation by forming a bulky associated species, $[SDS\text{-tetryl}]^{2-}$, which has a lower charge density than tetryl itself and, hence, a slightly longer migration time. The other two anionic analytes, TNT and TNB, appear to have little or no interaction with the negatively-charged SDS, and basically migrate as free anions. For CTAB, electrostatic attraction between the surfactant and anionic analytes promotes the formation of associated species CTAB-TNT, CTAB-TNB, and CTAB-tetryl. Since each of the associated species are neutral, the observed separation times for the analytes (Fig. 3b) are longer than those obtained in the presence of SDS (Fig. 3c) or in the absence of surfactant addition (Fig. 3a).

A mixture containing 2 mg/l of 13 different explosives and explosive derivatives (see experimental section) was prepared and analyzed on the microchip. Because of the high order of chemical selectivity displayed by the reaction with base, only TNT, TNB and tetryl form colored products under these buffer conditions and are detectable by microchip CE. Based on a minimum detectable signal-to-noise ratio of 3:1, in all cases, nonaqueous electrolyte containing 1.0 mM SDS gave the highest sensitivity, with detection limits as follows: TNT, 160 µg/l; TNB, 60 µg/l and tetryl, 200 µg/l.

The analysis of explosives in real world samples such as soil, groundwater or seawater, requires the incorporation of a sampling step in order to pre-concentrate or, in the case of soil, extract the explosives into a manageable liquid medium. For explosives, this has been accomplished very efficiently utilizing solid phase extraction. In order to demonstrate the direct applicability of the nonaqueous based microchip technique discussed here to SPE, we investigated the ex situ solid phase extraction of an

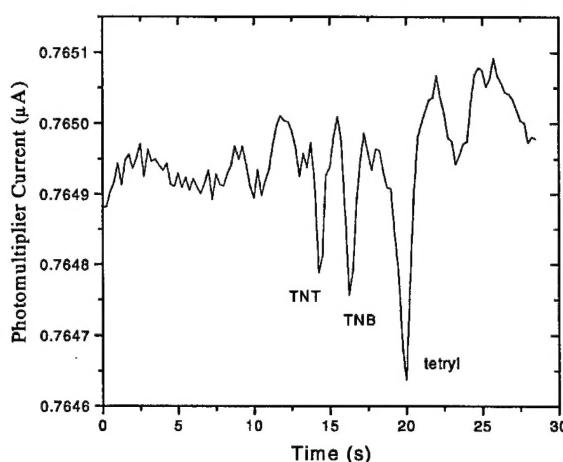


Fig. 5. Electropherogram of an SPE sample in MeCN/MeOH (87.5/12.5 (v/v)) containing 2.5 mM NaOH and 1 mM SDS, derived from a seawater sample spiked with 0.5 µg/l of each compound TNT, TNB, and tetryl. Applied separation field strength, -506 V/cm, using a 10 s floating load.

explosives mixture of 0.5 µg/l TNT, TNB and tetryl in seawater. Seawater is a matrix of interest to the Navy in the detection of buried land mines. A mini-column was prepared from the solid phase extractant, Lichrolut, and utilized for preconcentrating the three trinitroaromatics from a 40 ml seawater sample spiked with 0.5 µg/l of each trinitroaromatic into a 17 µl MeCN/MeOH nonaqueous sample for introduction to the microchip. Fig. 5 is the electropherogram obtained on the microchip following this SPE. The detection limits observed following SPE were as follows: TNT, 0.34 µg/l; TNB, 0.25 µg/l and tetryl, 0.19 µg/l. Actual concentration enhancements observed are detailed as follows: TNT, 470 times; TNB, 240 times and tetryl, 1050 times. The use of MeCN as both the eluting solvent as well as the running buffer for the CE microchip separation clearly offers a great advantage by avoiding sample dilution and consequent decreases in the overall concentration enhancements observed.

4. Conclusions

By utilizing nonaqueous electrolyte in the presence of low concentrations of surfactants, we have succeeded in selectively detecting and separating three trinitroaromatic explosives from a mixture of

13 explosives or explosive derivatives in less than 20 s via microchip CE. The compatibility of this system to SPE techniques was demonstrated, with trinitroaromatic explosives being detected at levels as low as 0.19–0.34 µg/l in seawater. Work is currently in process to enable on-line SPE of explosives in seawater, coupling samples directly to the microchip for rapid separation and detection of trinitroaromatic explosives.

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References

- [1] J. Wang, B. Tian, E. Sahlin, *Anal. Chem.* 71 (1999) 5436.
- [2] S.R. Wallenborg, C.G. Bailey, *Anal. Chem.* 72 (2000) 1872.
- [3] A. Hilmari, J.H.T. Luong, *Anal. Chem.* 72 (2000) 4677.
- [4] R. Foster, C.A. Fyfe, *Rev. Pure Appl. Chem.* 16 (1966) 61.
- [5] P. Buck, *Angew. Chem., Int. Ed. Engl.* 8 (1969) 120.
- [6] M.J. Strauss, *Chem. Rev.* 70 (1970) 667.
- [7] J. von Meisenheimer, *Liebigs Ann. Chem.* 323 (1902) 205.
- [8] C.L. Jackson, R.B. Earle, *Am. Chem. J.* 29 (1903) 89.
- [9] E. Buncel, A.R. Norris, K.E. Russell, R.J. Tucker, *J. Am. Chem. Soc.* 94 (1972) 1646.
- [10] C.A. Fyfe, C.D. Malkiewich, S.W.H. Damji, A.R. Norris, *J. Am. Chem. Soc.* 98 (1976) 6983.
- [11] R.T. Medary, *Anal. Chim. Acta* 258 (1992) 341.
- [12] I. Liska, *J. Chromatogr. A* 885 (2000) 3.
- [13] T.F. Jenkins, P.H. Miyares, K.F. Myers, E.F. McCormick, A.B. Strong, *Anal. Chim. Acta* 289 (1994) 69.
- [14] R.D. Oleschuk, L.L. Shultz-Lockyear, Y. Ning, D.J. Harrison, *Anal. Chem.* 72 (2000) 585.
- [15] J.P. Kutter, S.C. Jacobson, J.M. Ramsey, *J. Microcol. Sep.* 12 (2000) 93.
- [16] F.-M. Matysik, *Electrochim. Acta* 43 (1998) 3475.
- [17] J.L. Miller, M.G. Khaledi, D. Shea, *Anal. Chem.* 69 (1997) 1223.
- [18] J.H.T. Luong, A. Hilmari, A.-L. Nguyen, *J. Chromatogr. A* 864 (1999) 323.
- [19] S.-M. Hosseini, T. Tang, D.J. Harrison, *J. Am. Chem. Soc.* 119 (1997) 8716.
- [20] J.P. Kutter, S.C. Jacobson, N. Matsubara, J.M. Ramsey, *Anal. Chem.* 70 (1998) 3291.
- [21] P.B. Wright, A.S. Lister, J.G. Dorsey, *Anal. Chem.* 69 (1997) 3251.
- [22] G.E. Collins, Q. Lu, *Sens. Actuators B* 76 (2001) 244.
- [23] G.E. Collins, Q. Lu, *Anal. Chim. Acta* 436 (2001) 181.
- [24] Q. Lu, G.E. Collins, *Analyst* 126 (2001) 429.
- [25] C.F. Bernasconi, *J. Am. Chem. Soc.* 92 (1970) 129.
- [26] Y. Walbroehl, J.W. Jorgenson, *Anal. Chem.* 58 (1986) 479.
- [27] E.S. Sandra, J.P. Foley, *J. Chromatogr. A* 680 (1994) 73.
- [28] R.M. Seifar, J.C. Kraak, W.T. Kok, *Anal. Chem.* 69 (1997) 2772.